Reductive Electrochemical Silylation† of Unsaturated Nitrogen Functionalities: A Simple and Efficient Synthesis of Precursors of Bis(trimethylsilyl)methylamine

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Received May 16, 1994®

Synthesis of the title compound, **1**, *via* the electroreductive silylation of a series of unsaturated nitrogen derivatives, *i.e.*, trialkylsilyl cyanides, dimethylcyanamide, *tert*-butyl isocyanide bis(trimethylsilyl)carbodiimide, and trimethylsilyl isocyanate, is described in this paper. This process involves the use of an undivided cell, a sacrificial anode, and a constant current density. It gives yields comparable with those obtained in the previously described chemical route and appears to be safer and more economical.

Introduction

The utility of bis(trimethylsilyl)methylamine, **1** (BSMA), in organic synthesis, namely for the easy introduction of the)CHN(fragment into organic frameworks, has been well illustrated by the synthesis, in particular, of 2-aza 1,3-dienes,[1] 1,2-dihydroisoquinolines,[2] and bicyclic β-lactams.[3,4] We have recently described two chemical processes (A and B, respectively) for preparing **1**[2,5] (Scheme 1), one of which (A) uses the chmeical reductive silylation of trimethylsilyl cyanide.[5,6] However, since using lithium sand is expensive and relatively dangerous on a large scale on the one hand (method A) and bis(trimethylsilyl)chloromethane is not readily available (method B) on the other, the search for a simpler, safer, less expensive and easily applicable large scale process becomes apparent.

Choice of the Method

Electrochemical synthesis, using the technique developed in particular by Périchon,[7] has led to excellent results in our laboratories in other domains.[8] It could be an elegant alternative to our problem. By using intensiostatic equipment, an undivided cell, and a sacrificial anode[8b,9] made of an easily oxidizable metal, this technique offers numerous advantages over other electrolytic methods.[10] In particular, the use of an undivided cell avoids many difficulties related to the use of membranes:[7] ohmic drop, diffusion problems, and poor compatibility with organic solvents. In such a process, the anodic reaction tolerates the production of nucleophilic species at the cathode. Oxidation of an anode made with an electropositive metal such as aluminum avoids the oxidation, for example, of chloride ions released from chlorosilanes at the cathode[8] and, consequently, halogenation reactions in solutions which occur with a platinum anode.[10b] Moreover, as the anodic metal chloride (*i.e.*, $AlCl_3$) is formed during the reaction, the need for a supporting electrolyte is reduced to a minimum for starting the electrolysis. The reaction proceeds at room temperature. The electrochemical reactions involved are given in Scheme 2.

Tetrabutylammonium bromide was used as the supporting electrolyte, with a mixture of hexamethylphosphoramide (HMPA) and tetrahydrofuran (THF) as the solvent and a stainless steel grid as the cathode. The charge to be used was determined by the number of electrons required by the envisioned reaction. In any

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† Throughout this paper, silylation refers to trimethylsilylation.

® Abstract published in *Advance ACS Abstracts*, August 1, 1994.

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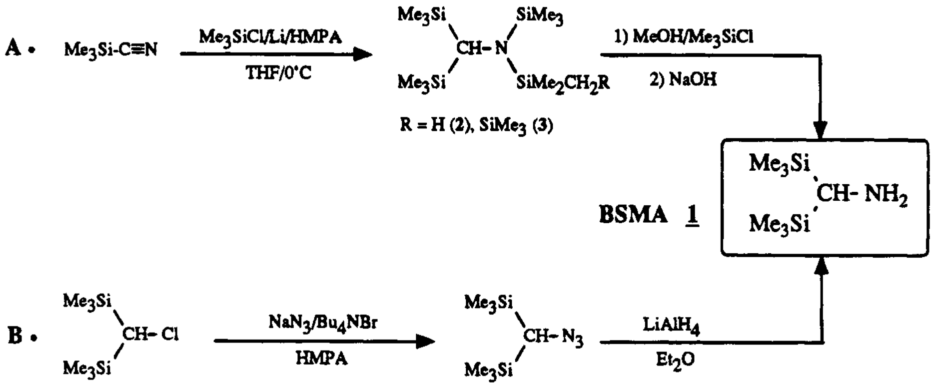
Scheme 1. Preparations of BSMA, 1, through Chemical Processes



Scheme 2. Electrochemical Reductive Silylation of Organic Substrates

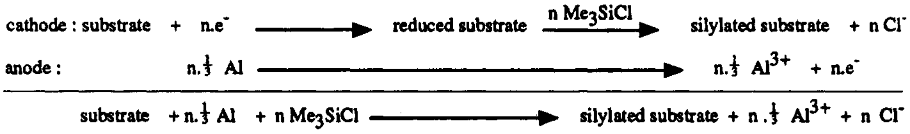


Table 1. Reductive Electrochemical Silylation of Me_3SiCN. Influence of the Respective Amounts of Me_3SiCl and HMPA

entry	process	Me_3SiCl[a]	HMPA[a]	2 + 3 yield (%)	2/3 ratio
1	A[b]	40	8	80	17/83
2	E[c]	15	3	75	10/90
3	E[c]	15[d]	1[d]	78	5/95
4	E[c]	15	0.5	40	13/87

[a] Equivalents/1 equiv of silyl cyanide. [b] Chemical process A. [c] Electrochemical process. [d] Standard proportions selected.

case, to silylate a given substrate, this latter must be easier to reduce than the electrophilic reagent, Me_3SiCl, and the metallic salt formed during the course of the reaction.

Results

Trimethylsilyl Cyanide. In order to compare the chemical (A) and electrochemical (E) reductive silylation routes, we started our study with trimethylsilyl cyanide. Thus, 1 equiv of this cyanide was injected into a mixture of THF, tetrabutylammonium bromide, and variable amounts of trimethylchlorosilane and HMPA (Table 1). After having passed 4.4 F/mol of substrate[11] through the cell, compounds **2**–**4** were obtained (Scheme 3), as in A.[6]

Compound **4** was also formed in low yield (8%, as in A[6]). Polysilylated methylamines **2** and **3** were formed, however, in yields and proportions depending upon the conditions of the electrolysis, as indicated in Table 1. Particularly interesting is the fact that it was not necessary to use as much chlorosilane and HMPA as in the case of the chemical process, in order to obtain comparable yields (compare entries 2 and 3 with entry 1). However, when less than 1 equiv of HMPA was used, lower yields were obtained and passivation of the electrodes occurred, sometimes causing the reaction to stop. The same result was observed when less than 2 equiv of THF per mole of substrate was used.

Another observation was an increase of the **2**/**3** product ratio when the imposed current intensity was increased; that also caused an increase of the cell voltage and temperature of the reaction medium. Consequently, the **2** + **3** yield dropped, and byproducts, as for example, tris(trimethylsilyl)amine, were formed. For these reasons, a current intensity was chosen so that the reaction medium temperature was kept below 40 °C. As an indication, 100, 300, and 600 mA (0.1/0.3/0.6 A/dm^2) were the typical values of the current intensities (and densities) used when 0.01, 0.015, and 0.03 mol of substrate, respectively, was submitted to electrolysis.

As previously described, compound **2** can easily be separated from **3** by distillation, and these compounds, or their mixture, can be protolyzed to give the free amine, BSMA, **1** (97% yield).[6]

Other Cyanides and *tert*-Butyl Isocyanide. We previously studied the chemical reductive silylation (A) of various cyano and isocyano derivatives Σ-(CN)[6] in order to obtain more information on the mechanism of this reaction and, especially, to find precursors of BSMA cheaper than trimethylsilyl cyanide. For a comparison between A and E, these compounds were treated under the standard conditions as defined above (Table 1, entry 3). After 6.6 F/mol had been passed, the reaction was complete. Results are given in Table 2 with reference to the chemical route. Yields of compounds **2** + **3** were of the same magnitude, except for *tert*-butyl isocyanide, in which case the yield was lower (Table 2, entry 4). Compound **3**, more highly silylated than **2**, predominated, and the **2**/**3** ratio was completely inverted in the case of the isocyanide. Enediamine **5** was formed in low yield (5%) besides **2** and **3**, when the substrate was dimethylcyanamide: **5** was obtained as a single *E* isomer, as in the case of like compound **4**. It was completely destroyed, however, when treated successively by MeOH/Me_3SiCl and NaOH (unlike **4** which remained unaffected).

Trimethylsilyl Isocyanate (6a) and (Trimethylsilyl)carbodiimide (6b). These readily available unsaturated nitrogen derivatives were expected to be able to yield **2** and **3** through reductive silylation. Both have been treated chemically (A route) and electrochemically (E route, standard conditions).

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(11) Theoretically, reductive silylation of a silyl cyanide requires 4 F/mol (see ref 6, Schemes V and VI). However, due to loss of electrical energy due to the Joule effect, the reaction generally requires about a 10% excess of electricity.

Scheme 3. Reductive Electrochemical Silylation of Trimethylsilyl Cyanide

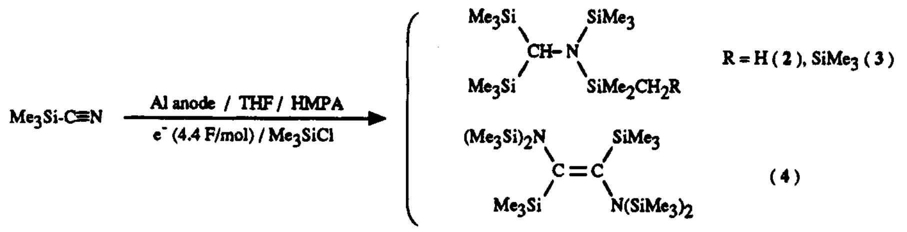
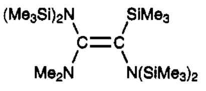


Table 2. Electrochemical Silylation of Σ-(CN)

$$\Sigma\text{-(CN)} \xrightarrow[\text{Me}_3\text{SiCl},^a\ e^- \ (5.5\ \text{F/mol})]{\text{Al anode, THF/HMPA}^a} \mathbf{2} + \mathbf{3} + \mathbf{5} + \Sigma\text{-SiMe}_3$$

entry	Σ-(CN)	**2 + 3** yield[b] (%)	**2/3** ratio[b] (%)	
1	$EtMe_2SiCN$	76 (85)	8/92 (22/78)	 (5)
2	*t*-$BuMe_2SiCN$	53 (57)	5/95 (58/42)	
3	Me_2NCN	65 (78)	9/91 (25/75)	
4	*t*-BuNC	43 (80)	16/84 (98/2)	

[a] Proportions of reactants are those defined at entry 3, Table 1. [b] Values in brackets refer to the A process.

Table 3. Reductive Silylation of Compounds 6a and 6b

$$\underset{\mathbf{6}}{\text{Me}_3\text{SiN=C=Z}} \xrightarrow[\text{silylation}]{\text{reductive}} \mathbf{2} + \mathbf{3} + \text{Z(SiMe}_3)_2$$

	2 + 3 yield (%)		**2/3** ratio (%)	
6	E	A	E	A
a (Z = O)	56	65.3	12/88	26/74
b (Z = $NSiMe_3$)	75	79	10/90	56/44

Electrochemical silylation of compounds **6a** and **6b** gave a **2** + **3** mixture (yields varying from moderate to good respectively) in which **3** is largely predominant (Table 3). Formation of tris(trimethylsilyl)amine (67% yield) from **6b** and hexamethyldisiloxane from **6a** was observed. The same observations were made when using the chemical process.

Conclusions

These results confirm that electrochemical silylation is an excellent alternative to the chemical route A, since equivalent yields were obtained using smaller amounts of solvents, very simple, easy-to-handle, and cheap equipment, and primarily, avoiding the use of an alkaline metal. Among the different precursors of BSMA that we have investigated, it is evident that dimethylcyanamide is the best because of its very low cost. For large scale preparation of BSMA, we recommend electrochemical silylation of dimethylcyanamide as the most practical synthetic method. Silyl isocyanate **6a** and bis(silyl)carbodiimide **6b** also could be good sources of BSMA.

Experimental Section

General Data. Gas chromatographic (GC) analyses were performed on a Hewlett-Packard 5890 (series II) temperature programmable (5 min at 50 °C, then 50−240 °C at 20 °c/min and finally 5 min at 240 °C) chromatograph equipped with capillary columns (CPSIL, 25 m × 0.32 mm × 0.25 μm). Infrared spectra were obtained using a Perkin-Elmer 1420 ratio recording infrared spectrophotometer and ^{1}H NMR spectra using a Hitachi R-1200 (60 mHz, solvent CCl_4 and CH_2Cl_2 at $\delta = 5.33$ ppm[12] as the internal reference) or a Bruker AC250 (250 MHz, solvent $CDCl_3$) or AC200 (200 MHz, solvent $CDCl_3$). These last two spectrometers were also used for recording ^{13}C and ^{29}Si NMR spectra. Most of the compounds obtained have been described in previous work.[6] All of the electrolyses were performed at room temperature under a dry argon atmosphere.

Starting Materials. Dimethylcyanamide, *tert*-butyl isocyanide, reagent-grade HMPA and THF, and tetrabutylammonium bromide (Lancaster) all were used without purification. Trimethylchlorosilane, kindly supplied by Rhône-Poulenc Co., was distilled over magnesium turnings prior to use and kept under an argon atmosphere. Trimethylsilyl cyanide (Fluka) was also obtained by reacting bis(trimethylsilyl)-sulfate[13] with dry potassium cyanide according to a preparation we have previously described.[14] Ethyldimethylsilyl cyanide, which can be obtained analogously, was best prepared by an exchange reaction between trimethylsilyl cyanide and ethyldimethylsilyl chloride in the presence of fluoride ions[15] (80% yield). Reaction of *tert*-butyldimethylsilyl chloride with dry potassium cyanide according to a reported procedure[16] afforded *tert*-butyldimethylsilyl cyanide in 76% yield. Trimethylsilyl isocyanate[17] (**6a**) and bis(trimethylsilyl) carbodiimide[18] (**6b**) were obtained via literature procedures.

Electrochemical Silylation Reactions. Electrolysis was performed, under magnetic stirring, in an undivided cylindrical cell.[7,8b,19] The sacrificial anode was an aluminum rod (*ca.* 8 mm diameter) and the cathode a stainless steel concentrically fitted cylindrical grid, both separated by a concentrically fitted plastic mesh to avoid any contact between them. The cell, containing a magnetic stirring bar, was connected with an argon inlet, a drying tube, and a bubbler. The constant current was provided by a Sodilec EPL 36-07 regulated DC power supply. This electrolytic equipment has already been described.[8b]

Into the cell (120 mL for 10 mmol) were successively introduced Bu_4NBr (50 mg), THF, HMPA, and Me_3SiCl in standard proportions (Table 1, entry 3). Any traces of hydrogen chloride (if any), which could result from the partial hydrolysis of Me_3SiCl by traces of water, was removed by a pre-electrolysis of the initial solution ($I = 1$ mA) for about 0.5 h (the end of the operation was indicated by the end of gas evolution at the bubbler). Then 10 mmol of the substrate was injected into the cell, and electrolysis was performed until the

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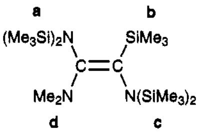
Table 4. NMR Data for Compound 5

	$^1H^a$	$^{13}C^a$	$^219Si^a$
	H_a: 0.24 (s, 18 H)	C_a: 4.9	Si_a: 5.31
		C_b: 4.3	
	H_b: 0.20 (s, 9 H)	C_c: 3.8	Si_b: −9.04
		C_d: 42.8	
	H_c: 0.21 (s, 18 H)	$=C_{ad}$: 156.4	
(5)	H_d: 2.69 (s, 6 H)	$=C_{bc}$: 115.7	Si_c: 0.53

[a] δ values in ppm downfield from internal TMS.

theoretically required charge had been passed. The contents of the cell then were transferred under inert gas into a 250-mL round-bottomed flask; the cell was rinsed with pentane (3 × 10 mL). Solvents and low-boiling materials were rotatory evaporated to yield a black-gray residue which was taken up in pentane (5 × 10 mL). The formed aluminum salts, which form an insoluble complex with HMPA, were removed by filtration. The organic layer was neutralized with aqueous sodium bicarbonate, washed with water (2 × 10 mL), and dried over Na_2SO_4. After evaporation of pentane, the residual bright-yellow oil was analyzed by GC and its constituents separated by distillation. For larger scale preparations, 0.15 and 0.3 mol of substrate were reacted in a 0.5 and 1 L cell,[8b] respectively.

Trimethylsilyl Cyanide. Starting from 1 g (0.01 mol) of this cyanide and after having passed 0.044 F, the final oil obtained (3.5 g) was analyzed by GC as a mixture of **2**, **3** and **4** in the proportions and yields indicated in Table 1 (entry 3). These compounds were separated by distillation and identified by comparison with reference products.[6] The same reaction was performed on a larger scale (0.15 mole, in a 0.5 L cell equipped with 6 anodes[8b]) with the same results.

Formation of tris(trimethylsilyl)amine occurred sometimes (mainly when the reaction temperature was above 35 °C). This compound was identified by comparison with a sample synthetized according to a reported procedure.[20]

Other Cyanides. Under the same conditions, other silyl cyanides led to the formation of the **2** + **3** mixture in the yields and proportions given in Table 2 (entries 1 and 2). Concurrently, disilanes $EtMe_2SiSiMe_3$ and t-$BuMe_2SiSiMe_3$ were formed in quantitative yields (92 and 89%, respectively). They were identified by comparison with authentic samples we have prepared.[21,22] Compound **4** or one of its homologues [for instance: $(Me_3Si)_2NC(SiMe_3)=C(SiMe_2R)N(SiMe_3)_2$, R = Et, *t*-Bu] were not detected.

Dimethylcyanamide. Following the general procedure, 0.7 g (0.01 mol) of this compound was electrolyzed (0.055 F), and 2.7 g of a mixture of **2**, **3**, and **5** was obtained. After separation of **2** + **3** (Table 2, entry 3), distillation left a crystalline compound (2.5 mg) which was recrystallized from ethanol (mp 178 °C) and identified by ^1H, ^{13}C, and ^{29}Si NMR (Table 4).

(Trimethylsilyl)dimethylamine was identified in the pentane extract from the reaction mixture by comparison of its GC retention time and its mass spectrum with those of an authentic sample.[23]

***tert*-Butyl Isocyanide.** As above, 0.055 F was necessary for the reductive silylation of 0.83 g (0.01 mol) of this substrate. Yields (not optimized) and the **2**/**3** ratio are given in Table 2 (entry 4). Also formed in the reaction was *tert*-butyltrimethylsilane. It was identified in the mixture at the end of the reaction by comparison of its GC retention time and mass spectrum with those of an authentic sample.[24]

Trimethylsilyl Isocyanate (6a). Chemical Process A. In a 1 L three-necked flask maintained in an ice bath and equipped with a thermometer, a magnetic stirring bar, an argon inlet, and a dropping funnel connected to a BaO drying tube were successively introduced lithium (3.43 g, 0.49 g atom, wire cut in small rods, ~5 mm³), Me_3SiCl (465 mL, 4.3 mol), and THF (250 mL). This mixture was stirred at 0 °C for 30 min. Then 5.6 g (0.049 mol) of **6a** dissolved in HMPA (85 mL, 0.49 mol) was added slowly, dropwise, with stirring to the cold mixture. The temperature was kept at 0 °C for 2 h and left for 12 h to return to 20 °C. Pentane (100 mL) was added to the reaction mixture in order to precipitate a large part of the salts (LiCl/HMPA complex). After filtration on a sintered glass funnel, and evaporation of the solvents (pentane, THF) and low-boiling materials (mainly excess of Me_3SiCl), the organic layer was taken up in pentane, washed with water, dried over sodium sulfate, and concentrated on a rotatory evaporator. Distillation of the yellow, oily residue (10.8 g) afforded a **2** + **3** mixture (63.5% yield, **2**/**3**: 26/74). No trace of tris(trimethylsilyl)amine[20] was detected by GC analysis of the reaction mixture.

Electrochemical Process E. Isocyanate **6a** (10.15 g, 0.01 mole) was reacted following the general procedure using 6.6 F/mol. Compounds **2** and **3** were obtained in the yields and proportions given in Table 3. Chromatographic (GC) analysis of the reaction mixture did not show formation of tris(trimethylsilyl)amine, but hexamethyldisiloxane was present.

Bis(trimethylsilyl)carbodiimide (6b). Chemical Process A. Using the equipment mentioned above, 3.7 g (0.02 mol) of **6b** was mixed at 0 °C with lithium (1.4 g, 0.2 g atom), Me_3SiCl (100 mL), and THF (65 mL) and the mixture stirred until no gas evolution occurred (if any). Then HMPA (36 mL) dissolved in THF (10 mL) was added dropwise during 30 min. The reaction mixture was stirred at 0 °C for 12 h. After the usual workup, 5 g of a crude mixture of **2** + **3** (79% yield, 56/44) and tris(trimethylsilyl)amine[20] (67% yield) was obtained (GC analysis).

If the free amine BSMA is desired, there is no need to separate the tris(trimethylsilyl)amine as, although it is reported difficult to hydrolyze even under acidic, homogeneous conditions,[25] it was readily and quantitatively cleaved by methanol in the presence of 1 equiv of Me_3SiCl to yield methoxytrimethylsilane and ammonium chloride (Scheme 4).

Scheme 4. Protolysis of Tris(trimethylsilyl)amine

$$(Me_3Si)_3N + Me_3SiCl \xrightarrow{MeOH} 3\ MeOSiMe_3 + NH_4Cl$$

Electrochemical Process E. Carbodiimide **6b** (1.86 g, 0.01 mol) was silylated following the already mentioned procedure using 6.6 F/mol. Compounds **2** and **3** were obtained in yields and proportions indicated in Table 3 (75%, 10/90), and tris(trimethylsilyl)amine was formed in a 60% yield.

Acknowledgment. Partial support of this study by the European Economic Community (Project SC1 CT 91/0646) and the Conseil Régional d'Aquitaine (Fonds de Coopération Aquitaine-Euskadi, no. 501081) is gratefully acknowledged. We wish to thank Prof. C. Biran (Laboratoire de Chimie Organique et Organométallique, Université Bordeaux I) for fruitful discussions and advice relating to electrochemical synthesis and S. Goizet and Ch. Bibes for their technical assistance.

OM940367A

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